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PHOTOCHEMICAL OXIDATION OF KRAFT AIR POLLUTANTS

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Maine University

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16. ABSTRACT

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N-isopropyl-S-benzylsulfenamide was found to undergo an unusual thermal elimination to form N-isopropylbenzalimine.

Lithium amides were found to form sulfenamides upon reaction with disulfide.

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CONCLUSIONS

The photolysis in air of the Kraft air pollutants methyl mercaptan and dimethyl disulfide results in rapid destruction of these compounds with formation of sulfur compounds in higher oxidation states. A number of the intermediates formed are subject to further photooxidation. It is likely that long term photooxidation of both pollutants will result in methanesulfonic acid and sulfur trioxide, two photochemically stable substances, as final sulfur containing products. Further work at lower concentrations and with longer wave length radiation will be necessary before extrapolation to atmospheric photochemistry will be possible.

INTRODUCTION

As a conservative estimate, more than three hundred thousand tons of reduced sulfur compounds are released into the atmosphere of the United States each year by Kraft pulping operations. The bulk of the malodorous compounds present in this effluent is known[1,2] to be hydrogen sulfide, methyl mercaptan (MM), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS). It has been the goal of a number of investigations to devise means of controlling the emission of these objectionable compounds; studies in this direction have included black liquor oxidation[3], catalytic oxidation[4], thermal gas phase oxidation[5], chlorination[2], and ozonation[2]. The condition of the air near any Kraft pulping operation bears ample evidence that the problem yet remains unsolved. A further related area still inadequately investigated concerns the fate of these prodigious quantities of reduced sulfur compounds upon being exposed to natural irradiation in the lower atmosphere.

Recently F.E. Murray of the Chemical Engineering Department of The University of British Columbia published the findings of his research[3,6] which indicated that photochemical oxidation of Kraft effluent holds some potential as a means of air pollution control. He was able to demonstrate photooxidation of methyl mercaptan, dimethyl disulfide, and dimethyl sulfide at both 2537Å and 3600Å. By monitoring the disappearance of starting material, he showed that DMDS undergoes photooxidation most rapidly, while DMS was found to be least reactive. In addition, MM exposed to solar radiation was found to disappear with a half-life of *ca* 7 days during a period with an average noon temperature of 10°C. Although Murray has provided useful information concerning the rate profiles for disappearance of MM, DMDS, and DMS under several irradiation conditions, little evidence for the types of products formed has been presented. In the case of DMS, for example, it was mentioned that SO_2 was shown to be present by mass spectroscopic analysis. This analysis, we feel, must surely have been far from complete, since SO_2 formation indicates extensive C-S bond fragmentation in DMS. At the time we initiated our study of this system, it seemed to us highly probable that non-sulfur-containing products would be present in addition to other sulfur-containing oxidation products, including SO_3, a known[7] photooxidation product of SO_2.

There are a number of earlier studies which have a bearing on the

possible consequences of exposing DMS, DMDS, and MM to ultraviolet light. Horner[8] has identified a large array of products including CH_4, C_2H_6, $(CH_3)_2S_2$, $CH_3SSC_2H_5$, $CH_3SCH_2SCH_3$, $CH_3SCH_2SCH_2SCH_3$, $CH_3SCH_2SSCH_3$, $CH_3SCH_2CH_2SCH_3$, $CH_3SCH_2CH_2SCH_3$, $CH_3SCH_2CH_2SSCH_3$, and $CH_3SCH_2SCH_2CH_3$ which are produced upon photolysis of DMS. The formation of these compounds can be explained if one assumes formation of methyl radicals and methanethiyl radicals upon light absorption, followed by a series of abstractions, coupling and addition reactions, i.e.

$$CH_3SCH_3 \xrightarrow{h\nu} CH_3S\cdot + CH_3\cdot$$

$$CH_3S\cdot + CH_3\cdot \text{ (or } R\cdot) \rightarrow CH_4 \text{ (or RH)} + CH_2 = S$$

$$CH_3S\cdot + CH_2 = S \rightarrow CH_3S - CH_2 - S\cdot$$

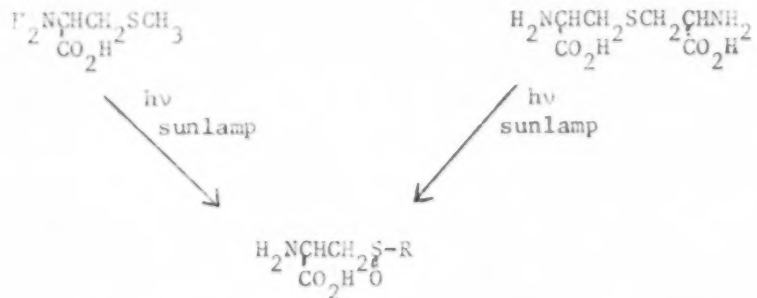
$$CH_3SCH_2S\cdot + CH_3\cdot \rightarrow CH_3SCH_2SCH_3$$

etc.

In addition, photosensitization can play a role in the photochemistry of DMS. Lossing[9] has shown that $Hg(^3P_2)$ sensitized photolysis results in formation of methane, thioformaldehyde, methyl mercaptan, and dimethyl disulfide.

Only a limited amount of work has been published on photooxidation of organic sulfides. Laarhoven[10] found that more than 80% conversion of dibenzyl sulfide to dibenzyl sulfoxide could be achieved by passing N_2 containing traces of O_2 through a solution of dibenzyl sulfide in alcohol while subjecting the solution to irradiation.

The photolysis of the sulfides, S-methyl cysteine (I) and lanthionine (II) in aqueous solution containing O_2 has been investigated[11] with the following results:



Since it has been shown[12] that more than one route exists for the formation of singlet oxygen in polluted atmospheres, it is pertinent to point

out also the recent finding of Foote[13] that singlet oxygen smoothly oxidizes sulfides according to:

$$2RSR + O_2 \xrightarrow[sens.]{h\nu} 2RS(O)-R$$

There have also been numerous studies of the photochemistry of mercaptans and disulfides[14]. Although none of these has involved detailed product studies upon photolysis in air, they do have a mechanistic bearing on the expected transformations in an atmospheric system. For example, Steer and Knight[15] have shown that methyl mercaptan undergoes photolysis to yield dimethyl disulfide, H_2, H_2S, and methane. Kinetic and trapping experiments indicated a primary process forming methanethiyl radicals followed by recombination to yield dimethyldisulfide. Fragmentations of a "hot" dimethyldisulfide molecule upon collision with methyl mercaptan was thought to produce the $CH_3\cdot$ and $\cdot SH$ radicals, precursors to the methane and hydrogen sulfide. In a related study, photolysis of dimethyldisulfide vapor was examined by Rao, Copeck and Knight[16] who concluded that the primary process involves S-S bond cleavage to form hot methanethiyl radicals. The major observable products were methyl mercaptan and polymeric material.

We have exposed DMS to high energy ultraviolet irradiation (200W Hanovia High Pressure Hg lamp) in air at 24°C and have observed 91% conversion in 6.63 hours to a product aerosol[17]. In spite of the complexity of the mixture we were able to identify, using a combination of chromatographic, spectroscopic and wet chemical methods, eleven products. Quantitatively, we were able to account for over 70% of the products. A summary of the results is presented in Table I.

The products indicate that likely major intermediates are $CH_3\cdot$ and $CH_3S\cdot$ formed by photochemical rupture of the C-S bond in DMS. Several of the products observed are also expected to yield these fragments upon photolysis, adding to the complexity of the system. The methyl radicals generated in the photooxidation of acetone[18] results in formation of CH_3OH, CH_2O, and HCO_2H in agreement with our studies. We also identified methyl formate in the product mixture which is interesting since it could conceivably be formed by either an ionic acid catalyzed esterification of formic acid by methanol or by combination of methyl and formate radicals in either the gas or condensed phase.

TABLE I

Products of DMS Photolysis at 24 ± 2°C.

Initial quantity of DMS = 1.36×10^{-2} moles. % conversion = 91 ± 4%.

Sulfur-Containing Products			Non-Sulfur-Containing Products		
Product	Moles	Moles Relative to Moles DMS Reacted	Product	Moles	Moles Relative to Moles DMS Reacted
$CH_3SO_2SCH_3$	0.37×10^{-3}	0.03	CH_3OH	1.18×10^{-3}	0.10
$CH_3\overset{O}{\overset{\|}{S}}SCH_3$	1.93×10^{-3}	0.16	HCO_2CH_3	0.18×10^{-3}	0.01
$CH_3\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-CH_3$	0.085×10^{-3}	0.007	HCO_2H	2.11×10^{-3}	0.17
CH_3SO_3H	2.57×10^{-3}	0.21	CH_2O	1.77×10^{-3}	0.14
CH_3SSCH_3	0.05×10^{-3}	0.004			
SO_2	0.94×10^{-3}	0.08			
SO_3	2.74×10^{-3}	0.22			

The sulfur containing products doubtlessly arise from a number of different pathways. The DMDS, which surely undergoes further photochemical transformations, probably forms at least in part by combination of $CH_3S\cdot$ radicals:

$$SCH_3S\cdot \rightarrow CH_3SSCH_3$$

The formation of CH_3SO_3H could occur via this radical also, i.e.

$$CH_3S\cdot + O_2 \quad CH_3SOO\cdot \xrightarrow{RH} CH_3SOOH$$

$$CH_3SOOH \xrightarrow{h\nu} CH_3SO\cdot + \cdot OH$$

$$CH_3SO\cdot \xrightarrow{RH} CH_3SOH$$

Further oxidation of methanesulfenic acid would yield methanesulfonic acid (CH_3SO_3H) possibly via methanesulfinic acid (CH_3SO_2H). It should be pointed out however that the sequence is speculative. Several known disproportionation reactions may accomplish similar results, e.g.

$$3CH_3SO_2H \rightarrow CH_3SO_2SCH_3 + CH_3SO_3H \text{ (ref. 19) } \underline{\text{or}}$$

$$5CH_3SOH \rightarrow CH_3SO_3H + 2CH_3SSCH_3 + H_2O \text{ (ref. 20).}$$

Further, a concurrent or alternate pathway into the sulfonic acid system may be via dimethylsulfoxide (DMSO). DMSO could be initially formed by photooxidation of DMS:

$$CH_3SCH_3 \xrightarrow[O_2]{h\nu} CH_3\overset{O}{\overset{\|}{S}}-CH_3$$

Recently, Gollnick and Stracke[20] found that photolysis at 2537Å of DMSO in degassed H_2O yields methane, CH_3SCH_3, $CH_3SO_2CH_3$, $CH_3SO_2SCH_3$, and CH_3SSCH_3, a product distribution similar to our own. We also however detected SO_2 and SO_3 in the sulfur containing group. If their contention is correct that the products are formed via CH_3SO_2H, then our observation of SO_2 as a DMS photooxidation product probably means that SO_2 results from breakdown of $CH_3SO_2\cdot$, possibly as a "hot" intermediate rather than by photolysis of CH_3SO_2H. Sulfur trioxide could then occur by the known photooxidation of SO_2. Our failure to detect methane could be due to the rapid trapping of $CH_3\cdot$ by O_2.

The above qualitative description of possible pathways, which at this stage are of course highly speculative, point out the multiplicity of routes available to account for the observed products and underscores the high complexity of this system.

METHODS

Photolysis was conducted in a 12.4 l pyrex round-bottom flask fitted with a water-cooled quartz lamp housing, a thermometer, and a stopcock fitted with a septum inlet. For introduction of the gas, methyl mercaptan, a manometric gas metering system was used rather than injection via the septum as was the case with liquid materials. The temperature of the system was controlled to $\pm$2 degrees by rapid pumping of thermostatted water through the quartz lamp housing and also cascading it over the reaction flask.

Gas chromatography-mass spectroscopy was done with an F & M Model 810 F.I.D. Gas Chromatograph interfaced with a DuPont Model 491 Mass Spectrometer. The GLC was equipped with either a 6 ft. 30% Triton-X305/ chromosorb W 30/60 column or a 5 ft. SE-30 on chromosorb P 45/60.

Nuclear magnetic resonance spectra were obtained with a Varian A-60 nmr spectrometer.

RESULTS AND DISCUSSION

A. Photolysis of Methyl Mercaptan (MM) in Air.

Photolysis of methyl mercaptan (20.1mm) in air (1 atm) with a 200 W high pressure mercury lamp at 32 $\pm$ 2° C for 50 minutes resulted in greater than 99% reaction of MM. The major product formed was dimethyl disulfide (51%) with methanesulfonic acid (CH_3SO_3H) also present in 17% yield. In addition, we have identified lesser quantities of ethyl mercaptan (C_2H_5SH), methanol (CH_3OH), formic acid (HCO_2H), methane (CH_4), sulfur trioxide (SO_3), and sulfur dioxide (SO_2). Other unidentified compounds are also present. Several of the compounds formed in our earlier photolysis of dimethyl sulfide, namely dimethylsulfoxide ($CH_3-\overset{O}{\overset{\|}{S}}-CH_3$), methylmethanethiolsulfonate ($CH_3SO_2SCH_3$), and dimethylsulfone ($CH_3SO_2CH_3$) were not formed in detectable quantities in the photolysis of MM in air. The present results are explicable in terms of a primary process involving S-H bond cleavage to form the $CH_3S\cdot$ radical which is sequentially oxidized to CH_3SO_3H possibly via intermediates CH_3SO, $CH_3SO_2\cdot$ and $CH_3SO_3\cdot$. Loss of SO_2 or SO_3 from the latter two intermediates would yield observed products. The known photooxidation of SO_2 to SO_3 could also be taking place. The small amounts of CH_3OH, HCO_2H, and CH_4 are possibly formed via a $CH_3\cdot$ radical resulting from competing C-S bond cleavage in CH_3SH.

We have conducted some photolysis runs on methyl mercaptan in air using the 200W mercury lamp filtered with Pyrex (3000Å cutoff). Although such a system represents greater intensity than sunlight, the high energy cutoff occurs at very close to the same energy. With CH_3SH initially at 20mm in 1 atmosphere of air, we find that 40% of the mercaptan is reacted after 48 hours at 32°C. This is substantially slower than we found with the unfiltered lamp, but the products thus far identified--dimethyl disulfide, methanesulfonic acid, methanol, and sulfur trioxide--nonetheless indicate similar extensive bond fragmentation and oxidation.

B. Photolysis of Dimethyl Disulfide (DMDS) in Air.

Photolysis of DMDS (0.5 ml) in air (12.4 l) with a 200W high pressure mercury lamp at 32 $\pm$ 2°C for 105 minutes resulted in approximately

50% reaction of DMDS. Major products formed were methylmethanethiolsulfonate ($CH_3SO_2SCH_3$) and methanesulfonic acid. The presence of methanesulfinic acid (CH_3SO_2H) was implied by identification of methyl methanesulfinate in the photolysis product mixture after reaction with diazomethane.

Other compounds demonstrated to be present in the photolysis mixture were methyl formate (HCO_2CH_3), S_8, SO_2, and SO_3. We were unable to detect MM in the product mixture. Other presently unidentified products are also present as photolysis products.

These results indicate probable formation of $CH_3S\cdot$ as a first intermediate followed by further oxidation. Methyl methanethiolsulfonate may be formed by either direct photooxidation of DMDS without S-S bond rupture or by combination of the intermediate free radicals $CH_3SO_2\cdot$ and $CH_3\dot{S}$. Since photolysis of MM yielded DMDS as a major product, it follows that compounds such as $CH_3SO_2SCH_3$ and S_8 must be eventual products of MM photolysis even though they were not detected after the short term photolysis of MM.

C. Photolysis of Intermediates.

Methyl methanethiolsulfonate (MMTS) a product we found in the earlier dimethyl sulfide photooxidation studies absorbs UV radiation at 280 mμ. We expected it to be photochemically active and thus only an intermediate under long-term photooxidation of dimethyl sulfide. Studies of the photochemical behavior of this compound were begun under AP00383-06 (with I.B. Douglass) and have been continued under R-800209.

Our initial studies have been conducted in degassed tetrahydrofuran. Using GC, NMR, and wet chemical techniques we have found that MMTS undergoes 62% reaction in 7 hours in oxygen-free THF at room temperature to yield methane, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, methanesulfinic acid (CH_3SO_2H), methanesulfonic acid (CH_3SO_3H), and sulfur dioxide. The products can be accounted for by the following sequence of reactions:

$$CH_3\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-SCH_3 \xrightarrow{h\nu} CH_3\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}\cdot + CH_3S\cdot$$

$$2CH_3S\cdot \rightarrow CH_3SSCH_3$$

$$CH_3S\cdot \xrightarrow{RH} CH_3SH$$

$$CH_3SO_2\cdot \rightarrow CH_3\cdot + SO_2$$

$$CH_3\cdot \xrightarrow{RH} CH_4$$

RH = eg.

$$CH_3SO_2\cdot \xrightarrow{RH} CH_3SO_2H$$

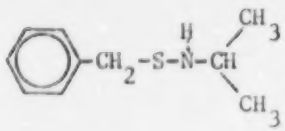
$$3CH_3SO_2H \rightarrow CH_3SO_3H + CH_3\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-SCH_3 + H_2O$$

The latter disproportionation, although rather astounding, is a known reaction which has been investigated by Kice.

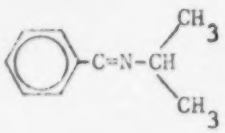
D. Other Fundamental Chemistry of Low-Molecular Weight Organosulfur Compounds.

(1) A Novel Sulfenamide Elimination.

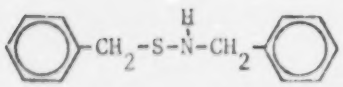
While attempting to purify two sulfenamides prepared by our recently discovered sulfenamide synthetic method, we discovered that both underwent a very unusual elimination reaction. Compound I when warmed under vacuum, yielded II; compound III under similar conditions yielded IV.



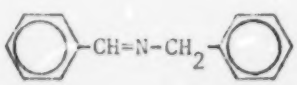
I.



II.



III.



IV.

This reaction was not observed with a number of other N,N-disubstituted sulfenamides prepared earlier. Some possible pathways (using I → II as an example) include:

$$Ar\text{-}CH_2\text{-}S\text{-}\ddot{N}H\text{-}R \rightarrow Ar\text{-}CH\text{-}\overset{\overset{S^-}{|}}{\overset{+}{N}}H\text{-}R \rightarrow ArCH\text{-}\overset{\overset{SH}{|}}{N}\text{-}R \rightarrow ArCH{=}NR + H_2S \quad \underline{OR}$$

$$ArCH_2\text{-}S\text{-}\overset{\overset{H}{|}}{N}\text{-}R \rightarrow Ar\text{-}\underset{-}{CH}\diagup\!\!\diagdown\overset{\overset{S}{\|}}{\underset{\underset{H}{|}}{\overset{+}{N}}}\text{-}R \rightarrow Ar\text{-}CH{=}S + RNH_2 \rightarrow ArCH{=}NR + H_2S$$

(2) A New Sulfenamide Synthetic Method.

The long used method for preparation of sulfenamides involves chlorination of a disulfide followed by aminolysis:

$$R\text{-}S\text{-}S\text{-}R + Cl_2 \rightarrow 2RSCl \xrightarrow{R'_2NH} R\text{-}S\text{-}NR'_2 + R'_2NH_2Cl$$

The yields are not high and one is faced with the unpleasant task of handling Cl_2 gas.

We have reported that the same transformation can be accomplished directly in higher yield by utilizing Ag^+ to labilize the S-S bond.

$$R\text{-}S\text{-}S\text{-}R \xrightarrow{Ag^+} (RSSR)Ag^+ \xrightarrow{R'_2NH} R\text{-}S\text{-}NR'_2 + R'_2NH_2^+ + AgSr$$

We have recently found that the disulfide-sulfenamide transformation can be accomplished in one operation by converting the amine to the more powerfully nucleophilic lithium salt:

$$R_2NH + nBuLi \xrightarrow[-78^\circ C]{Hexane} R_2\bar{N}Li^+ + nBuH$$

$$R_2\bar{N}Li^+ \xrightarrow[-78^\circ C]{R'SSR'} R_2N\text{-}SR' + LiSR$$

E. Mass Spectra of Thiolsulfonate Esters.

We have collaborated with Eric Block of the University of Missouri and Franklin Davis of Drexel University in a study of fragmentation patterns of thiolsulfonate esters and related compounds. The results of the work have been submitted by Prof. Block to the Journal of Organic Chemistry.

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